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# **Application of Inorganic Ion Exchangers to Metallurgy**

**By D. E. Shanks, E. G. Noble, A. M. Pierzchala,  
and D. J. Bauer**



**UNITED STATES DEPARTMENT OF THE INTERIOR**

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# UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	min	minute
cm	centimeter	mL	milliliter
g	gram	mL/hr	milliliter per hour
g/L	gram per liter	mL/min	milliliter per minute
hr	hour	pH	hydrogen-ion concentration (logarithm of reciprocal)
L	liter	ppm	part per million by weight
meq	milliequivalent	wt pct	weight percent
meq/g	milliequivalent per gram		
mg	milligram		

# APPLICATION OF INORGANIC ION EXCHANGERS TO METALLURGY

By D. E. Shanks,<sup>1</sup> E. G. Noble,<sup>2</sup> A. M. Pierzchala,<sup>2</sup> and D. J. Bauer<sup>3</sup>

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## ABSTRACT

The Bureau of Mines surveyed a variety of inorganic ion-exchange materials to determine their suitability for removing valuable accessory elements and troublesome contaminants from metallurgical process and waste streams. Most of the materials, which included molecular sieves, heteropolyacid salts, and hydrous metal oxides, did not give adequate separations, did not have the necessary stability in strong acids or bases, or were not in a physical form suitable for ion-exchange use. Many of the suitable inorganic materials, especially the hydrous oxides, were capable of cation exchange with high capacity only in basic conditions, which caused hydrolysis of most of the cations tested.

Multivalent anions, such as arsenate and phosphate, were easily removed from acidic solutions by hydrous oxides. Hydrous zirconia was the best material for this purpose. Multivalent anions were not easily desorbed because of compound formation; therefore, conventional ion-exchange techniques could not be employed. As an alternative approach, hydrous ferric hydroxide was used as a filter material to remove arsenate and phosphate from acid solutions. One gram of arsenic was removed from solution for each 20 g of ferric hydroxide. Ferric hydroxide is preferable to hydrous zirconia for use as a filter material because of low cost.

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## INTRODUCTION

Metallurgical process and waste streams contain valuable accessory elements and troublesome contaminants in very small concentrations. Most of these streams are strongly acidic or basic and with conventional processing must be neutralized before accessory elements or contaminants can be removed. Ion exchange is a common industrial method by which ions in dilute solution are concentrated in the solid ion-exchange matrix, but is seldom used in metallurgical applications because of the high cost and the fact that organic based ion-exchange resins are not sufficiently stable or do not give adequate separation factors in hostile environments found in many process streams.

Recent interest by radiochemists, spurred by a need to selectively remove elements from highly radioactive solutions, has revived research in inorganic ion-exchange materials. Many inorganic materials have been reported to act as ion exchangers under suitable circumstances. These materials, especially the hydrous oxides,<sup>4</sup> exchange anions from acidic solution and cations from basic solutions. Some are amphoteric and behave as anion exchangers at pH's lower than their isoelectric points and cation exchangers at higher pH's. This limits the effectiveness of the ion-exchange method to cations that do not precipitate in base and anions that do not decompose in acid. Many inorganic ion-exchange materials are stable in hostile environments, such as ionizing radiation, strong

salt solutions, or strong acids and bases. Some inorganic ion-exchange materials show high selectivity, which enables them to give complete separation.

There are hundreds of references on inorganic ion exchange, but the field is adequately described in two books and several review articles (4-6, 9, 21).<sup>5</sup> There are many ways of classifying the ion-exchange compounds. Amphlett (4) grouped the inorganic ion-exchange compounds into four groups: clay minerals, the zeolites, heteropolyacid salts, and hydrous oxides and insoluble salts. Most of the research in this field has been theoretical or analytical, and there have been few attempts to use inorganic ion exchangers in the metallurgical industry.

The objective of the Bureau of Mines research was to test a wide range of inorganic ion-exchange materials to determine if any could be used to selectively remove any of 21 cations and 3 anions from synthetic process streams. The goal was to find promising materials for research of a more specific nature, in which an effort would be made to selectively remove one or more elements from complex solutions with selected ion-exchange materials displaying good stability, high permeability for good column operation, and good selectivity to allow for high separation and concentration factors.

## INORGANIC COMPOUND SCREENING TESTS

Thirty-three inorganic compounds were screened for ion-exchange activity: (1) The hydrous oxides of titanium, iron, zirconium, and tin, (2) the ferrocyanides of chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, and lead, (3) molecular sieve types 3A, 4A, 5A, 13X, and SK-500, (4) aluminum hydroxy

sulfate, (5) the phosphates of titanium, zirconium, and cerium, (6) ceric titanate, (7) titanium vanadate, (8) the arsenates of zirconium and thorium, (9) ammonium molybdophosphate, and (10) the tungstates of titanium, zirconium, and cerium. Only the molecular sieves, ceric titanate, zirconium phosphate and ammonium molybdophosphate were obtainable

<sup>4</sup>The term "hydrous oxide" is assigned to oxide or hydroxide precipitates containing an undefined amount of bound water.

<sup>5</sup>Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

commercially.<sup>6</sup> All of the other compounds were synthesized from reagent-grade chemicals. Names only are given in the text for the inorganic ion-exchange compounds because most of them were complex substances formed by the hydrolysis and polymerization of hydrated salts. For example, hydrous zirconia is not wet  $ZrO_2$ , but a complex polymer, possibly made up of  $Zr(H_2O)_8^{4+}$  building blocks (26). When efforts were made to duplicate these compounds, no two were exactly the same and most were amorphous, which prevented identification by X-ray diffraction. The exact methods of synthesis are more meaningful than names or formulas. However, because of the large number of compounds synthesized, it is not possible to list them all. Table 1 lists text references in which the specific methods of synthesis can be found. In many cases, the ion-exchange activity was reported to be caused by waters of hydration and could be lost by heating above 100° C or aging. All samples were washed and dried at 40° C and promptly used.

Each substance was tested by shaking 200-mg portions for 8 hr with 10-mL solutions of water, 0.1N  $H_2SO_4$ , 0.1N HCl, or 0.1N NaOH containing the following ions, each at a concentration of 0.1N: Lithium, sodium, potassium, magnesium, calcium, vanadium ( $VO^{2+}$ ), chromium(III), ammonium, manganese(II), iron(III), cobalt(II), nickel(II), copper(II), silver, zinc, cadmium, mercury(II), aluminum, gallium, thallium, lead(II), phosphate, arsenate, and cyanide. Individual equilibration of the 33 potential ion-exchange compounds with each of the 24 ions in the 4 types of solutions involved 3,168 tests. Because of the large number of tests, 18-mL vials were racked in

TABLE 1. - Methods of ion exchanger synthesis

Exchanger	Reference <sup>1</sup>
Arsenates:	
Thorium.....	2, 27
Zirconium.....	7
Ferrocyanides:	
Cadmium.....	21
Chromium.....	18
Cobalt.....	23, 31
Copper.....	13
Ferric.....	15
Ferrous.....	15
Lead.....	21
Manganese.....	21
Nickel.....	16
Zinc.....	12
Hydrous oxides:	
Ferric hydroxide.....	17, 20, 22
Tin.....	10
Titanium.....	28
Zirconium.....	1, 26
Phosphates:	
Cerium.....	3
Titanium.....	14
Zirconium.....	19
Tungstates:	
Cerium.....	30
Titanium.....	25
Zirconium.....	8
Other:	
Aluminum hydroxy sulfate...	29
Titanium vanadate.....	24

<sup>1</sup>Numbers refer to items in the reference list.

<sup>6</sup>Reference to specific manufacturers, stock numbers, control numbers, or lot numbers is made for identification only and does not imply endorsement by the Bureau of Mines. There is a strong possibility that like-named products from other manufacturers or different batches from the same manufacturer would behave differently.

trays of 40 and agitated by a reciprocating shaker. One-milliliter aliquots were analyzed by induction coupled plasma-atomic emission spectroscopy (ICP/AES). Since many ions can be analyzed in the same sample, the number of samples was decreased to a manageable 924 by allowing the solids to settle, and combining 1-mL aliquots from the 24 different ionic solutions in each series into 7 compatible groupings: (1) ammonium ion, (2) lithium, potassium, gallium, vanadyl, cupric, and zinc ions, (3) magnesium, aluminum, calcium, chromic, manganous, cobaltous, and nickelous ions, (4) ferric, silver, cadmium, thallium, mercuric, sodium, and plumbous ions, (5) arsenate ion, (6) phosphate ion, and (7) cyanide ion.



The distribution coefficient,  $K_d$ , for each ion is defined as the number of milliequivalents of ion exchanged or adsorbed per gram of air-dried ion exchanger divided by the number of milliequivalents of the ion per milliliter of

final (equilibrium) solution. Since it is very difficult to determine concentration in the solid material,  $K_d$  was determined indirectly from the change in solution concentration by the formula

$$K_d = \frac{10(\text{beginning concentration, } N - \text{final concentration, } N)}{0.2(\text{final concentration, } N)}$$

The  $K_d$  for ions in water and 0.1N concentrations of HCl and H<sub>2</sub>SO<sub>4</sub> for the 33 compounds are shown in the appendix. Ions with  $K_d < 1$  were not listed. In most cases, the ions showing low  $K_d$  included alkali and alkaline earth elements and aluminum. Results were not listed for ions equilibrated with exchanger materials in basic solution because many of the ions hydrolyzed and precipitated and gave high values for  $K_d$ . A notable exception was the  $5 \times 10^2 K_d$  for Li<sup>+</sup> in 0.1N NaOH when equilibrated with aluminum hydroxy sulfate. Cyanide ion did not show significant adsorption in basic solution and decomposed in acid solution.

The capacities were determined on 23 of the ion-exchange materials by using the method described by Fisher and Kunin (11). In this method, cation capacity (milliequivalents cation-exchange capacity per gram of dry hydrogen form material) was determined by titrating the H<sup>+</sup> form of the ion-exchange material, which had been equilibrated in 0.1N NaOH, with 0.1N standard acid. The anion-exchange capacity was determined by equilibrating the chloride form of the material with a 4-wt pct sodium sulfate solution and titrating the equilibrated form with 0.1N silver nitrate. Table 2 shows the cation and anion capacities for 25 of

TABLE 2. - Ion-exchange capacity, milliequivalents per gram

Exchanger	Cation capacity	Anion capacity	Exchanger	Cation capacity	Anion capacity
Ferrocyanides:			Molecular sieves (commercial):		
Cadmium ferrocyanide on SiO <sub>2</sub> .....	0.5	0.3	3A <sup>1</sup> .....	3.0	1.3
Chromium.....	2.9	.2	4A <sup>2</sup> .....	5.3	.6
Cobalt.....	4.4	0	5A <sup>3</sup> .....	3.1	1.0
Copper.....	3.0	.3	13X <sup>4</sup> .....	5.8	ND
Ferric.....	4.0	.1	SK-500 <sup>5</sup> .....	1.3	ND
Ferrous.....	.5	.2	Phosphates:		
Lead.....	2.7	.3	Cerium.....	4.6	ND
Manganese.....	3.4	0	Commercial zirconium, ZP-1 <sup>6</sup> .....	10	ND
Nickel.....	2.9	.1	Zirconium.....	12	ND
Zinc.....	2.7	.3	Tungstates:		
Hydrous oxides:			Cerium.....	3.2	0
Tin.....	2.6	ND	Titanium.....	4.4	.1
Zirconium.....	2.4	1.3	Zirconium.....	3.8	.1

ND Not determined.

<sup>1</sup>4- to 8-mesh beads, potassium aluminosilicate.

<sup>2</sup>Activated, 8-12 mesh.

<sup>4</sup>Powder, sodium aluminosilicate.

<sup>3</sup>Activated, 1/8-inch pellets.

<sup>5</sup>One-sixteenth-inch pellets.

<sup>6</sup>Cation-exchange crystals, 20-50 mesh; Bio-Rad Laboratories (Richmond, CA), control No. 10481.

NOTE.--Reference to specific products does not imply endorsement by the Bureau of Mines.

the ion-exchange materials. Cation capacities ranged from 0.5 to 12 meq/g. The anion capacities ranged from 0 to 1.6 meq/g. The hydrous oxides were good anion exchangers with capacities of 1.0 to 1.6 meq/g, but most of the other materials were poor anion exchangers.

The solubilities were estimated by analyzing for the increase in exchanger elements in solution after equilibration or by noting the exchanger weight loss when equilibrated with acids and bases. Table 3 shows solubilities for 28 of the ion-exchange materials in water and 0.1N

TABLE 3. - Ion exchanger solubility, grams per liter

Exchanger material	0.1N HCl	0.1N H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O	0.1N NaOH
<b>Ferrocyanides:</b>				
Cadmium.....	1.4	2.0	2.6	
Chromium.....	.6	1.6	2.6	
Cobalt.....	1.9	2.6	2.0	
Copper.....	1.5	1.0	1.0	>20
Ferric.....	1.1	1.7	1.7	
Ferrous.....	.7	1.5	1.3	>20 in 1N
Lead.....	1.4	2.1	1.2	
Manganese.....	1.6	1.7	2.7	
Nickel.....	1.4	2.5	1.8	>20
Zinc.....	1.7	1.5	2.8	
<b>Hydrous oxides:</b>				
Tin.....	1.6	1.3	.7	
Titanium.....	1.8	.7	1.6	
Zirconium.....	.3	0	.2	
<b>Molecular sieves (commercial):</b>				
3A <sup>1</sup> .....	3.3	2.7	3.3	
4A <sup>2</sup> .....	2.9	2.6	.3	
5A <sup>3</sup> .....	3.1	>20	.6	
13X <sup>4</sup> .....	3.4	2.5	.2	
SK-500 <sup>5</sup> .....	4.3	5.3	.4	
<b>Phosphates:</b>				
Cerium.....	1.2	1.3 <sup>4</sup>	.6	
Commercial zirconium, ZP-1 <sup>6</sup> .	.8	.7	.9	
Titanium.....	.9	.9	.9	
Zirconium.....	.9	.3	1.5	
<b>Tungstates:</b>				
Cerium.....	1.7	2.3	2.1	
Titanium.....	1.0	.9	.4	
Zirconium.....	1.4	.8	.3	
<b>Other:</b>				
Commercial ammonium molybdophosphate <sup>7</sup> .....	ND	ND	ND	>20
Titanium vanadate.....	ND	2.4	ND	
Zirconium arsenate.....	2.1	.6	1.2	

ND Not determined.

<sup>1</sup>4- to 8-mesh beads, potassium aluminosilicate.

<sup>2</sup>Activated, 8-12 mesh.

<sup>3</sup>Activated, 1/8-inch pellets.

<sup>4</sup>Powder, sodium aluminosilicate.

<sup>5</sup>One-sixteenth-inch pellets.

<sup>6</sup>Cation-exchange crystals, 20-50 mesh; Bio-Rad, control No. 10481.

<sup>7</sup>Cation-exchange crystals, powder; Bio-Rad, catalog No. 146-2070, control No. 13827.

concentrations of HCl, H<sub>2</sub>SO<sub>4</sub>, and NaOH. Since the results are preliminary and all the compounds were not checked, more exacting solubility tests need to be made. The large increases in concentration of some ion exchanger matrix elements in solution indicate unacceptable dissolution. Most of the solubilities are much higher than reported in the literature and indicate that freshly prepared amorphous, hydrous materials are not as resistant to attack as aged, crystalline, well-dried or calcined materials. A good example is the difference in solubility between amorphous aluminum hydroxide gel and calcined alpha-alumina.

Very few of the substances were suitable for testing as inorganic ion exchangers. In most cases, the physical characteristics and  $K_d$ 's were poor and the solubilities were high. Slight, but difficult to control, changes in synthesis conditions lead to differences in the crystal form which strongly influence the selectivity of the materials toward elements or compounds. Thorium arsenate typifies the problems encountered. Thorium arsenate was evaluated because it was reported by Alberti (2) to be a good exchanger for lithium. On checking the  $K_d$  for different ions, it was poor for lithium, but was an excellent exchanger for vanadyl, aluminum, calcium, plumbous, thallium, and phosphate. X-ray diffraction examination showed that crystalline  $\text{Th}(\text{HAsO}_4)_2 \cdot 4\text{H}_2\text{O}$  was formed instead of the  $\text{Th}(\text{HAsO}_4)_2 \cdot \text{H}_2\text{O}$  Alberti produced. Solubility tests were

especially discouraging. Thorium arsenate has enormous pollution potential and must not be soluble to be potentially useful as an ion-exchange material; however, its solubility ranged from 0.21 wt pct of the sample in 0.1N HCl to 100 wt pct of the sample in 1N NaOH.

The molecular sieves adsorbed large quantities of most elements, so separation factors were low. Another problem was the high solubility in every solvent except water.

The ferrocyanides were also nonselective and too soluble in all solvents tested.

Ammonium molybdophosphate could only be used in acid solution, and was completely soluble in base solution. It showed moderate exchange for most cations and was an excellent exchange material for mercury, thallium, and lead. Anion exchange was poor.

Hydrous zirconia, titania, tin, and iron were excellent anion exchangers, but in most cases, poor cation exchangers. Hydrous zirconia was an excellent ion exchanger for phosphate and arsenate. Hydrous tin and titania were good for phosphate and arsenate. Hydrous iron was not as good as the tetravalent oxides for adsorbing phosphate and arsenate. Its solubility was higher, but it may be the preferred material because of its low cost.

#### IMPROVING THE PHYSICAL PROPERTIES OF INORGANIC COMPOUNDS

From the screening tests, the group of materials classified as hydrous oxides has the most potential for more extensive investigation with simulated process streams. One major drawback has to be overcome: The slimy, gelatinous nature of the products would make column applications impossible.

Several methods were investigated as possible ways of improving the physical properties of the exchange materials.

These included precipitation of the material onto a suitable substrate (such as carbon or silica), sol-gel encapsulation, reflux crystallization, and coagulating the gels followed by decrepitation to suitable particle size.

Impregnation or precipitation of inorganic ion-exchange materials onto either carbon or silica gel stabilized the ion exchangers in a form suitable for column operations. Flows were good and results

were reproducible, but capacities were very low, which made this technique useless for commercial application.

Sol-gel encapsulation is a technique by which the hydrous oxides can be emulsified with an organic liquid and then separated as beads suitable for column operation. Many combinations of organic liquids and emulsifiers were investigated. Although this was a promising approach, it was too complex for the time available for research. Sol-gel encapsulation needs to be more thoroughly investigated.

Some of the amorphous oxides were converted to crystalline form by refluxing

for 1 to 30 days, but the time periods were too long and reproducibilities were too poor to make them attractive as exchangers.

The only method that gave satisfactory results involved precipitation and coagulation with ammonium hydroxide, filtration or centrifugation, drying at 40° C, and washing the warm, dehydrated mass immediately in cold water to cause decrepitation. The relatively large chunks produced were washed with water and introduced into a column. Flow rates were fast, and surface area was adequate for uptake or exchange of ions.

#### SPECIFIC APPLICATIONS

The preliminary screening phase demonstrated that a thorough, long-term research commitment will be needed before any wide-range application can be found for inorganic ion exchangers in the metallurgical industry. Several specific applications that seemed feasible were pursued.

Hydrous oxides were effective in removing phosphate and arsenate from acidic solutions. An extensive literature search (1, 4-5, 9, 17, 20, 22) and the preliminary screening showed that hydrous zirconia and hydrous ferric hydroxide were the most promising oxides for anion-exchange applications. Zirconia was the most successful of the hydrous oxides for removing phosphate and arsenate from solution; however, iron, although not as effective as zirconium, was the logical choice for commercial application because of its low cost.

Most of the elements or compounds tested, other than arsenate and phosphate, were not amenable to inorganic ion exchange. Cyanide decomposes in the pH range where effective exchange can take place. Heavy-metal cations are not easily separated from the acidic solutions in which they are usually found. Most cations precipitate in basic

solution where ion exchange is expected. One exception was the separation of cobalt and nickel from ammonia solution with hydrous oxides.

#### HYDROUS ZIRCONIA

Replicate tests to produce hydrous zirconia were conducted by slowly sparging ammonia gas into 3 L of 0.07M zirconyl chloride at 20° C. The sparging was terminated when the pH was 7.0. The slurry was filtered or centrifuged, the wet solids were dried at 40° C, and reslurried in cold water to produce suitable size particles for column operation. Table 4 shows capacities and table 5 shows  $K_d$ 's for the tests conducted on four batches of freshly prepared hydrous zirconia.

TABLE 4. - Cation and anion capacities for four batches of hydrous zirconia, milliequivalents per gram

Batch	Cation capacity	Anion capacity
1.....	2.3	1.6
2.....	2.4	1.2
3.....	2.5	1.0
4.....	2.5	1.3
Average.....	2.4	1.3
Std. dev.....	±.1	±.3

TABLE 5. - Distribution coefficients of four batches of hydrous zirconia for arsenate and phosphate in selected acids and bases

(10<sup>-3</sup> K<sub>d</sub> in 0.1N solution)

Batch	HCl		H <sub>2</sub> SO <sub>4</sub>		H <sub>2</sub> O		NaOH	
	AsO <sub>4</sub> <sup>3-</sup>	PO <sub>4</sub> <sup>3-</sup>	AsO <sub>4</sub> <sup>3-</sup>	PO <sub>4</sub> <sup>3-</sup>	AsO <sub>4</sub> <sup>3-</sup>	PO <sub>4</sub> <sup>3-</sup>	AsO <sub>4</sub> <sup>3-</sup>	PO <sub>4</sub> <sup>3-</sup>
1.....	0.07	2	0.03	0.0	0.003	2	0.005	0.06
2.....	.02	.05	.006	.008	.004	5	.0001	.01
3.....	.05	2	.01	.03	.007	2	.003	.2
4.....	.03	.3	.009	.02	.003	.9	.001	.009
Avg.....	.04	1	.01	.02	.004	2	.002	.07
Std. dev....	±.02	±1	.01	±.01	±.002	±2	±.002	±.09

NOTE.--K<sub>d</sub> =  $\frac{10(\text{beginning concentration, } \underline{N} - \text{final concentration, } \underline{N})}{0.2(\text{final concentration, } \underline{N})}$ .

The capacities averaged 2.4 meq/g for cations and 1.3 meq/g for anions. The K<sub>d</sub>'s indicated a preference for arsenate in HCl and for phosphate in water and in HCl. However, the reproducibility was very poor.

Additional tests were performed in which synthesis temperatures were 20°, 40°, and 60° C and synthesis pH's were 5, 7, and 10. The results are summarized in table 6, which shows the variation in K<sub>d</sub> for arsenate and phosphate equilibrated with hydrous zirconia synthesized at 20° and 60° C and pH's of 5, 7 and 10. The data showed that K<sub>d</sub> for phosphate and arsenate are increased by increasing the synthesis temperature and pH during precipitation of hydrous zirconia with ammonia. This is a tentative conclusion because the deviations from average were large, even in replicate tests (table 5).

TABLE 6. - Effects of pH and temperature on the distribution coefficients of hydrous zirconia for arsenate and phosphate from 0.1N HCl solution

(Distribution coefficients, K<sub>d</sub> × 10<sup>-3</sup>)

pH	At 20° C		At 60° C	
	AsO <sub>4</sub> <sup>3-</sup>	PO <sub>4</sub> <sup>3-</sup>	AsO <sub>4</sub> <sup>3-</sup>	PO <sub>4</sub> <sup>3-</sup>
5.....	0.002	0.005	ND	ND
7.....	.04	.9	0.05	TA
10.....	.3	2	.9	TA

ND Not determined.

TA Total adsorption.

Since high-synthesis pH gave the best results, two selectivity tests were made with hydrous zirconia synthesized at 20° C by rapidly increasing the pH to more than 10 with concentrated NH<sub>4</sub>OH. Total adsorptions were obtained for phosphate and arsenate.

A large batch of hydrous zirconia for column tests was produced by direct addition of ammonium hydroxide into zirconyl chloride. Thirteen grams of hydrous zirconia was slurried and poured into a 1-cm-diam column. The solids settled to a depth of 12.7 cm. One column volume was 10 mL. A five-column-volume (50 mL) mixture of 0.06N H<sub>3</sub>AsO<sub>4</sub> and 0.05N H<sub>3</sub>PO<sub>4</sub>, containing 2.9 meq of arsenate and 2.5 meq of phosphate, was passed through the column at a rate of 4 mL/min. The arsenate and phosphate were totally adsorbed. The column was washed with water and eluted with 1N NaOH. Sodium hydroxide removed 80 wt pct of the arsenate and 62 wt pct of the phosphate in the first 10 column volumes (100 mL). There was some prolonged tailing that might have been due to removal of column materials, either by dissolution or physical means. The eluate contained 0.3 to 0.5 ppm zirconium. Efforts to elute phosphate or arsenate with dilute acids, bases, or strong anion solutions were not successful. Large excesses of arsenate would not elute phosphate and vice versa. This can be contrasted with an experiment in which 5.8 meq of arsenate was loaded on a column containing basic anion-exchange resin

in the chloride form. Only 75 wt pct of the arsenate loaded, but 100 wt pct was eluted from the column in 12 column volumes (120 mL) of 0.1N HCl. This wide contrast in behavior between the hydrous zirconia and the commercial anion-exchange resin indicates that arsenate and phosphate form compounds with the hydrous zirconia rather than adsorbing by an ion-exchange mechanism.

#### HYDROUS FERRIC HYDROXIDE

Gelatinous precipitates were formed by adding ammonium hydroxide to solutions of iron chlorides, nitrates, and sulfates. The best results were obtained with ferric sulfate. The procedure for producing hydrous ferric hydroxide consisted of precipitating a gelatinous amorphous product from 1 L of 0.1M ferric sulfate by mixing in 1.5 L of 1M ammonium hydroxide at room temperature and filtering through Whatman No. 1 paper. The gelatinous solids were reslurried in water and filtered. Most of the water

was first removed by centrifugation and decantation. The filter cake was dried at 40° C, reslurried in cold water, and filtered through Whatman No. 40 paper. Columns of the material were prepared by washing and decanting to remove the fines that would plug the column. The material was suspended in water and poured into 1-cm-diam columns to a consolidated solids depth of 25 cm. The average loading of the column was approximately 20 g of material.

The adsorption of 0.004N arsenate was investigated at room temperature for two flow rates, 50 and 600 mL/hr. There was no breakthrough of arsenate from either the fast- or slow-flow experiments after the passage of 8 L of arsenate solution. Total loading was 1.04 g arsenic per 20 g of exchanger material and gave a capacity of >2.1 meq/g for arsenate.

#### HYDROUS ALUMINA

Cobalt and nickel ammine complexes were separated on hydrous alumina. A column was prepared by washing acidic aluminum oxide ( $\text{Al}_2\text{O}_3$ )<sup>7</sup> with water, decanting the fines, and pouring the coarse fraction into a 1-cm-diam column to a consolidated solids depth of 17 cm. Ten milliliters of 2.3M ammonium sulfate  $[(\text{NH}_4)_2\text{SO}_4]$  solution containing 0.07 meq cobalt and 0.01 meq nickel were loaded on the column. The cobalt and nickel were eluted from the column with 2.3M  $(\text{NH}_4)_2\text{SO}_4$ . Figure 1 shows the separation of cobalt and nickel on hydrous alumina.

Sixty weight percent of the nickel eluted with the first 20 mL of eluate, and all of the nickel was eluted in 50 mL. The first cobalt was collected in the 60- to 70-mL fraction of eluate with a peak in the 110- to 120-mL fraction and then tailing out to 400 mL.

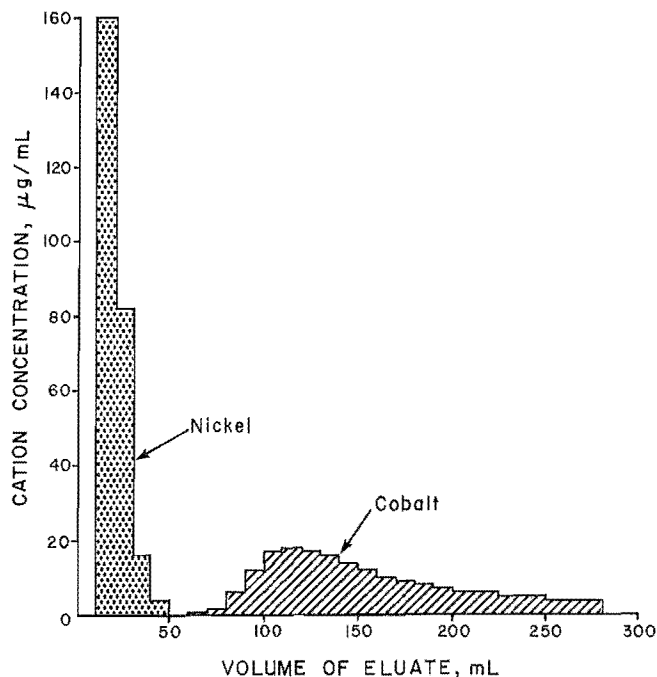


FIGURE 1. - Separation of cobalt and nickel on hydrous alumina.

<sup>7</sup>Alfa Products, Inc. (Danvers, MA), stock No. 87222, lot 080675.

## SUMMARY AND CONCLUSIONS

Inorganic ion exchange showed potential for some specific metallurgical and waste stream separations. The original intent of the study was to survey the field of inorganic ion exchange, to determine the best potential materials, and apply these materials to metallurgical separations.

Changes in inorganic ion exchanger synthesis conditions too subtle to be controlled or observed in the bench-scale experiments led to vastly different ion-exchange properties in the product. Aging increased the stability of the materials but decreased their ion-exchange capability, probably through loss of water of hydration and an accompanying decrease in surface area. These differences prevented a large number of comparative tests from being conducted over long periods of time using a single preparation. Emphasis was shifted to finding solutions to a few specific problems.

A very preliminary study with readily available hydrous alumina demonstrated that separation was possible for the cobalt-nickel ammine complexes, even though the distribution coefficients for cobalt and nickel were zero under all of the conditions tested, and hydrous alumina was not necessarily the best inorganic ion exchanger for this purpose.

Extensive testing demonstrated that both hydrous zirconia and hydrous ferric hydroxide had high affinities for phosphate and arsenate ions. Arsenic is a problem element in some hydrometallurgical applications. Although arsenate can be easily removed from acidic solutions with hydrous oxides, there are some major problems that need additional research.

It is very difficult to desorb phosphate and arsenate from hydrous oxides because large excesses of most anions will not replace the phosphate and arsenate; 0.5N to 1.0N NaOH is needed. This extreme treatment leads to degradation of the exchanger. The necessity for the strong eluant indicates that the phosphate and arsenate uptake are due to compound formation rather than ion exchange. The only practical application for these exchangers would be to use the hydrous oxides as filter materials to remove arsenic. Since the kinetics are slow and the materials are not completely inert, the cheapest materials would have to be used. Although hydrous ferric hydroxide is not as effective as hydrous zirconia in removing arsenate from solution, it is much less expensive, and it is innocuous if only small amounts were lost to the environment.

Despite the many papers to the contrary, very few of the multivalent elements are adsorbed in a true ion-exchange reaction. Because of strong adsorption, slow kinetics, lack of reproducibility, and poor stability in acids and bases, inorganic materials need to be investigated as filters to remove certain compounds from waste or bleed stream. Because of the higher costs of handling the material on a one-time batch basis rather than regenerating it, cheap natural materials would be preferable to synthesized compounds; for example, clays, zeolites, brucite, and goethite. Longer term research is required to utilize sol-gel or crystallization techniques to decrease the solubility of the hydrous gels and enhance the handling characteristics.

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## APPENDIX

## Distribution coefficients

Distribution coefficients were calculated by the formula

$$K_d = \frac{10(\text{beginning concentration, } \underline{N} - \text{final concentration, } \underline{N})}{0.2(\text{final concentration, } \underline{N})}$$

from data collected as described on pages 2-6. Because of wide variability in the data, only one significant figure was justified for each entry. This was achieved by dividing each distribution coefficient by 1,000. All distribution coefficients of 10,000 or higher were called "total adsorption" (TA). Thirty-three inorganic compounds were tested for ion-exchange activity. Most of these were synthesized just prior to use.

TABLE A-1. - Distribution coefficients ( $K_d$ ) multiplied by  $10^{-3}$ 

Ion	H <sub>2</sub> O	0.1N HCl	0.1N H <sub>2</sub> SO <sub>4</sub>	Ion	H <sub>2</sub> O	0.1N HCl	0.1N H <sub>2</sub> SO <sub>4</sub>
HYDROUS TITANIA				HYDROUS TIN OXIDE			
Ag <sup>+</sup> ...	0.01	ND	ND	Ag <sup>+</sup> ...	0.02	P	P
AsO <sub>4</sub> <sup>3-</sup> ...	TA	TA	0.2	AsO <sub>4</sub> <sup>3-</sup> ...	TA	1	0.6
Cr <sup>3+</sup> ...	.02	ND	ND	Cd <sup>2+</sup> ...	.02	.002	.005
Ga <sup>3+</sup> ...	.2	ND	ND	Cu <sup>2+</sup> ...	.03	.004	.01
Hg <sup>2+</sup> ...	.9	ND	ND	Hg <sup>2+</sup> ...	TA	P	.1
Pb <sup>2+</sup> ...	.05	ND	ND	Pb <sup>2+</sup> ...	TA	P	P
PO <sub>4</sub> <sup>3-</sup> ...	TA	TA	TA	PO <sub>4</sub> <sup>3-</sup> ...	TA	TA	TA
VO <sup>2+</sup> ...	.3	ND	ND	VO <sup>2+</sup> ...	.01	.003	.003
				Zn <sup>2+</sup> ...	.02	.002	.003
HYDROUS ZIRCONIA				CADMIUM FERROCYANIDE ON SILICA GEL			
Al <sup>3+</sup> ...	0.01	0	0	Ag <sup>+</sup> ...	0.5	P	P
AsO <sub>4</sub> <sup>3-</sup> ...	TA	TA	TA	Co <sup>2+</sup> ...	.03	0.03	0.03
Cr <sup>3+</sup> ...	.02	0	0	Cu <sup>2+</sup> ...	.03	.01	.02
Cu <sup>2+</sup> ...	.01	.003	.002	Fe <sup>3+</sup> ...	P	.02	.001
Fe <sup>3+</sup> ...	.03	0	.003	Ga <sup>3+</sup> ...	.02	.02	.02
Ga <sup>3+</sup> ...	.1	0	0	Hg <sup>2+</sup> ...	.01	P	.02
Pb <sup>2+</sup> ...	.01	P	0	Mn <sup>2+</sup> ...	.01	.006	.006
PO <sub>4</sub> <sup>3-</sup> ...	TA	TA	TA	NH <sub>4</sub> <sup>+</sup> ...	.02	.01	.01
VO <sup>2+</sup> ...	3	0	0	Ni <sup>2+</sup> ...	.02	.02	.02
				Pb <sup>2+</sup> ...	.03	P	P
				Tl <sup>+</sup> ...	.01	P	.006
				VO <sup>2+</sup> ...	.02	.03	.04
				Zn <sup>2+</sup> ...	.03	.03	.03
COBALT FERROCYANIDE				COPPER FERROCYANIDE ON CHARCOAL			
Ag <sup>+</sup> ...	6	P	P	Ag <sup>+</sup> ...	0.4	P	P
Al <sup>3+</sup> ...	.05	0.01	0.01	Al <sup>3+</sup> ...	.02	0	0
Cd <sup>2+</sup> ...	.1	.04	.1	AsO <sub>4</sub> <sup>3-</sup> ...	.1	.003	.002
Cr <sup>3+</sup> ...	.02	.002	.002	Cr <sup>3+</sup> ...	.01	.002	.001
Cu <sup>2+</sup> ...	1	1	1	Fe <sup>3+</sup> ...	.2	0	0
Ga <sup>3+</sup> ...	TA	.2	.2	Ga <sup>3+</sup> ...	.07	0	0
Hg <sup>2+</sup> ...	.01	P	.02	Hg <sup>2+</sup> ...	.2	P	.09
Mn <sup>2+</sup> ...	.02	.01	.01	PO <sub>4</sub> <sup>3-</sup> ...	TA	0	.02
NH <sub>4</sub> <sup>+</sup> ...	.5	.4	.5	VO <sup>2+</sup> ...	.3	0	.001
Ni <sup>2+</sup> ...	.2	.2	.2				
Pb <sup>2+</sup> ...	.05	P	P				
Tl <sup>+</sup> ...	TA	P	TA				
VO <sup>2+</sup> ...	.6	1	.5				
Zn <sup>2+</sup> ...	1	.4	.5				
CHROMIUM FERROCYANIDE				FERRIC FERROCYANIDE			
Al <sup>3+</sup> ...	0.01	0	0	Ag <sup>+</sup> ...	0.2	P	P
Ga <sup>3+</sup> ...	.03	0	0	Al <sup>3+</sup> ...	.01	0	0
NH <sub>4</sub> <sup>+</sup> ...	.009	.009	.01	AsO <sub>4</sub> <sup>3-</sup> ...	0	.01	.004
				Ga <sup>3+</sup> ...	.03	.001	.003
				PO <sub>4</sub> <sup>3-</sup> ...	.04	.01	0
				VO <sup>2+</sup> ...	.01	.004	.004

ND Not detected.

P Precipitated.

TA Total adsorption.

TABLE A-1. - Distribution coefficients ( $K_d$ ) multiplied by  $10^{-3}$ --Continued

Ion	H <sub>2</sub> O	0.1N HCl	0.1N H <sub>2</sub> SO <sub>4</sub>	Ion	H <sub>2</sub> O	0.1N HCl	0.1N H <sub>2</sub> SO <sub>4</sub>
FERROUS FERROCYANIDE				NICKEL FERROCYANIDE			
Ag <sup>+</sup> ....	0.02	P	P	Ag <sup>+</sup> ....	0.03	P	P
NH <sub>4</sub> <sup>+</sup> ...	.01	0.007	0.003	Cd <sup>2+</sup> ...	.01	0.01	0.01
Tl <sup>+</sup> ....	.4	P	.1	Ga <sup>3+</sup> ...	.01	.001	0
LEAD FERROCYANIDE				MANGANESE FERROCYANIDE			
Ag <sup>+</sup> ....	0.1	P	P	Ag <sup>+</sup> ....	0.2	P	P
Al <sup>3+</sup> ...	.01	0	0	AsO <sub>4</sub> <sup>3-</sup> ...	.06	0	0
AsO <sub>4</sub> <sup>3-</sup> ...	.04	.006	.006	Cd <sup>2+</sup> ...	.08	.04	.07
Cd <sup>2+</sup> ...	.03	.04	.06	Co <sup>2+</sup> ...	.06	.06	.2
Co <sup>2+</sup> ...	.01	.02	.2	Cu <sup>2+</sup> ...	.02	.07	.1
Cu <sup>2+</sup> ...	.04	.05	.03	Hg <sup>2+</sup> ...	.02	P	.03
Ga <sup>3+</sup> ...	.08	.02	.03	NH <sub>4</sub> <sup>+</sup> ...	0	.007	.01
Hg <sup>2+</sup> ...	.008	P	.02	Ni <sup>2+</sup> ...	.01	.05	.1
Mn <sup>2+</sup> ...	.003	.003	.05	Tl <sup>+</sup> ....	.01	P	.02
NH <sub>4</sub> <sup>+</sup> ...	.01	.009	.02	VO <sup>2+</sup> ...	.007	.02	.03
Ni <sup>2+</sup> ...	.01	.02	.1	Zn <sup>2+</sup> ...	.04	.04	.05
Tl <sup>+</sup> ....	.005	P	.01				
VO <sup>2+</sup> ...	.03	.03	.1				
Zn <sup>2+</sup> ...	.04	.04	.04				
ZINC FERROCYANIDE				MOLECULAR SIEVE 3A <sup>1</sup>			
Ag <sup>+</sup> ....	1	P	P	Ag <sup>+</sup> ....	TA or P	P	P
Al <sup>3+</sup> ...	.01	0	0	AsO <sub>4</sub> <sup>3-</sup> ...	0.002	.2	TA
AsO <sub>4</sub> <sup>3-</sup> ...	.001	.01	.005	Ca <sup>2+</sup> ...	2	0	0.006
Cu <sup>2+</sup> ...	.05	.03	.03	Cd <sup>2+</sup> ...	TA or P	.07	.08
Li <sup>+</sup> ....	.01	.001	.002	Co <sup>2+</sup> ...	TA or P	.03	.04
NH <sub>4</sub> <sup>+</sup> ...	.01	.002	.007	Cr <sup>3+</sup> ...	TA or P	.06	.1
Tl <sup>+</sup> ....	.01	P	.006	Cu <sup>2+</sup> ...	TA or P	.05	.07
VO <sup>2+</sup> ...	.02	.01	.01	Fe <sup>3+</sup> ...	TA or P	.2	.2
				Ga <sup>3+</sup> ...	.9	.6	2
				Hg <sup>2+</sup> ...	.2	P	.1
				Li <sup>+</sup> ....	.08	.009	.01
				Mg <sup>2+</sup> ...	4	0	0
				Mn <sup>2+</sup> ...	TA or P	.05	.05
				NH <sub>4</sub> <sup>+</sup> ...	.2	.009	.01
				Ni <sup>2+</sup> ...	TA or P	.01	.01
				Pb <sup>2+</sup> ...	TA or P	P	.1
				PO <sub>4</sub> <sup>3-</sup> ...	0	.6	TA
				Tl <sup>+</sup> ....	TA	P	P
				VO <sup>2+</sup> ...	.01	.08	.09
				Zn <sup>2+</sup> ...	TA or P	.04	.06

P Precipitated.

TA Total adsorption.

<sup>1</sup>4- to 8-mesh beads, potassium aluminosilicate.

TABLE A-1. - Distribution coefficients ( $K_d$ ) multiplied by  $10^{-3}$ --Continued

Ion	H <sub>2</sub> O	0.1N HCl	0.1N H <sub>2</sub> SO <sub>4</sub>	Ion	H <sub>2</sub> O	0.1N HCl	0.1N H <sub>2</sub> SO <sub>4</sub>
MOLECULAR SIEVE 4A <sup>1</sup>				MOLECULAR SIEVE 5A <sup>2</sup>			
Ag <sup>+</sup> ....	TA	P	P	Ag <sup>+</sup> ....	TA	P	P
Al <sup>3+</sup> ...	0.2	0	0	AsO <sub>4</sub> <sup>3-</sup> ...	0.005	0.9	3
AsO <sub>4</sub> <sup>3-</sup> ...	.004	.3	TA	Cd <sup>2+</sup> ...	TA or P	.008	.008
Ca <sup>2+</sup> ...	5	.007	.02	Co <sup>2+</sup> ...	1	.003	.002
Cd <sup>2+</sup> ...	6	.08	.07	Cr <sup>3+</sup> ...	TA or P	.03	.04
Co <sup>2+</sup> ...	9	.06	.05	Cu <sup>2+</sup> ...	TA or P	.003	.005
Cr <sup>3+</sup> ...	TA or P	.09	.1	Fe <sup>3+</sup> ...	TA or P	.9	1
Cu <sup>2+</sup> ...	9	.06	.1	Ga <sup>3+</sup> ...	TA	TA	.8
Fe <sup>3+</sup> ...	.8	.3	.4	Hg <sup>2+</sup> ...	2	P	1
Ga <sup>3+</sup> ...	.6	.4	TA	K <sup>+</sup> ....	.2	.001	0
Hg <sup>2+</sup> ...	.3	P	.3	Li <sup>+</sup> ....	.02	.005	.005
K <sup>+</sup> ....	.6	0	.003	Mg <sup>2+</sup> ...	.02	.002	.006
Li <sup>+</sup> ...	.05	.006	.007	Mn <sup>2+</sup> ...	.7	.003	.002
Mg <sup>2+</sup> ...	2	0	0	NH <sub>4</sub> <sup>+</sup> ...	.2	.001	.004
Mn <sup>2+</sup> ...	1	.06	.06	Ni <sup>2+</sup> ...	1	.005	.003
NH <sub>4</sub> <sup>+</sup> ...	0.3	.007	.01	Pb <sup>2+</sup> ...	TA	P	0
Ni <sup>2+</sup> ...	6	.03	.03	PO <sub>4</sub> <sup>3-</sup> ...	.005	TA	.005
Pb <sup>2+</sup> ...	3	P	0	Tl <sup>+</sup> ....	6	P	.006
PO <sub>4</sub> <sup>3-</sup> ...	0	.8	TA	VO <sup>2+</sup> ...	.04	.02	.02
Tl <sup>+</sup> ....	TA	P	.2	Zn <sup>2+</sup> ...	TA or P	.007	.005
VO <sup>2+</sup> ...	.007	.09	.1				
Zn <sup>2+</sup> ...	TA or P	.05	.09				
MOLECULAR SIEVE 13X <sup>3</sup>				MOLECULAR SIEVE SK-500 <sup>4</sup>			
Ag <sup>+</sup> ....	TA or P	P	0	Ag <sup>+</sup> ....	0.1	P	P
AsO <sub>4</sub> <sup>3-</sup> ...	0	1	2	AsO <sub>4</sub> <sup>3-</sup> ...	.009	0.003	0.03
Ca <sup>2+</sup> ...	.4	0	0	Cd <sup>2+</sup> ...	.05	.005	.005
Cd <sup>2+</sup> ...	TA or P	.02	.03	Co <sup>2+</sup> ...	.04	.005	.005
Co <sup>2+</sup> ...	TA or P	.008	.008	Cr <sup>3+</sup> ...	.7	.01	.007
Cr <sup>3+</sup> ...	TA or P	.04	.05	Cu <sup>2+</sup> ...	.04	0	0
Cu <sup>2+</sup> ...	TA or P	.01	.01	Ga <sup>3+</sup> ...	TA	.01	.002
Fe <sup>3+</sup> ...	.6	.6	.7	Hg <sup>2+</sup> ...	.3	P	.06
Ga <sup>3+</sup> ...	TA	TA	TA	K <sup>+</sup> ....	.05	.01	.009
Hg <sup>2+</sup> ...	8	P	1	Mn <sup>2+</sup> ...	.03	.003	0
K <sup>+</sup> ....	.08	.008	.01	NH <sub>4</sub> <sup>+</sup> ...	.02	0	0
Li <sup>+</sup> ....	0.09	.006	.006	Ni <sup>2+</sup> ...	.04	.001	.002
Mg <sup>2+</sup> ...	TA	.002	.001	Pb <sup>2+</sup> ...	.2	P	P
Mn <sup>2+</sup> ...	TA or P	.006	.004	PO <sub>4</sub> <sup>3-</sup> ...	.1	.2	.08
NH <sub>4</sub> <sup>+</sup> ...	.005	TA	TA	Tl <sup>+</sup> ....	.1	P	.02
Ni <sup>2+</sup> ...	TA or P	.008	.008	VO <sup>2+</sup> ...	.01	.003	0
Pb <sup>2+</sup> ...	TA	P	P	Zn <sup>2+</sup> ...	.04	0	0
PO <sub>4</sub> <sup>3-</sup> ...	.005	TA	TA				
Tl <sup>+</sup> ....	TA	P	.2				
VO <sup>2+</sup> ...	.04	.02	.03				
Zn <sup>2+</sup> ...	TA or P	.01	.01				

P Precipitated.

TA Total adsorption.

<sup>1</sup>Activated, 8-12 mesh.<sup>2</sup>Activated, 1/8-inch pellets.<sup>3</sup>Powder, sodium aluminosilicate.<sup>4</sup>One-sixteenth-inch pellets.

TABLE A-1. - Distribution coefficients ( $K_d$ ) multiplied by  $10^{-3}$ --Continued

Ion	H <sub>2</sub> O	0.1N HCl	0.1N H <sub>2</sub> SO <sub>4</sub>	Ion	H <sub>2</sub> O	0.1N HCl	0.1N H <sub>2</sub> SO <sub>4</sub>
TITANIUM PHOSPHATE				FRESHLY PREPARED ZIRCONIUM PHOSPHATE			
Ag <sup>+</sup> ....	0.01	P	P	Ag <sup>+</sup> ....	.03	P	P
Al <sup>3+</sup> ...	.02	0.003	0.003	Al <sup>3+</sup> ...	.4	0	.02
AsO <sub>4</sub> <sup>3-</sup> ..	.04	.3	.2	AsO <sub>4</sub> <sup>3-</sup> ..	.08	.3	.2
Cd <sup>2+</sup> ...	.01	.001	0	Ca <sup>2+</sup> ...	.03	0	0
Cr <sup>3+</sup> ...	.02	0	0	Cd <sup>2+</sup> ...	.05	0	0
Fe <sup>3+</sup> ...	.05	.02	.06	Co <sup>2+</sup> ...	.03	0	0
Ga <sup>3+</sup> ...	.03	.007	.02	Cr <sup>3+</sup> ...	.09	0	0
Hg <sup>2+</sup> ...	.3	P	.03	Cu <sup>2+</sup> ...	.1	.003	.004
K <sup>+</sup> .....	.01	.004	.005	Fe <sup>3+</sup> ...	TA or P	.2	.3
Pb <sup>2+</sup> ...	.07	P	P	Ga <sup>3+</sup> ...	TA	.04	.05
Tl <sup>+</sup> .....	.03	P	.01	Hg <sup>2+</sup> ...	1	P	0
VO <sup>2+</sup> ...	.03	.002	.004	K <sup>+</sup> .....	0.07	0.02	0.02
				Mg <sup>2+</sup> ...	.02	0	0
				Mn <sup>2+</sup> ...	.04	0	0
				NH <sub>4</sub> <sup>+</sup> ...	.03	0	.01
				Ni <sup>2+</sup> ...	.03	0	0
				Pb <sup>2+</sup> ...	1	P	P
				Tl <sup>+</sup> .....	.1	P	.04
				VO <sup>2+</sup> ...	.3	.01	.01
				Zn <sup>2+</sup> ...	.05	.002	0
COMMERCIAL ZIRCONIUM PHOSPHATE, ZP-1 <sup>1</sup>				TITANIUM VANADATE			
Ag <sup>+</sup> ....	0.04	P	P	Ag <sup>+</sup> ....	.3	P	P
Al <sup>3+</sup> ...	.1	0.03	0.02	Al <sup>3+</sup> ...	.05	0	0
AsO <sub>4</sub> <sup>3-</sup> ..	.01	.05	.04	AsO <sub>4</sub> <sup>3-</sup> ..	ND	8	ND
Ca <sup>2+</sup> ...	.05	0	0	Ca <sup>2+</sup> ...	.03	0	.003
Cd <sup>2+</sup> ...	.1	.002	.003	Cd <sup>2+</sup> ...	.03	0	.001
Co <sup>2+</sup> ...	.05	0	0	Co <sup>2+</sup> ...	.03	.001	.003
Cr <sup>3+</sup> ...	.1	0	0	Cr <sup>3+</sup> ...	1	.006	.01
Cu <sup>2+</sup> ...	.2	.02	.01	Cu <sup>2+</sup> ...	.04	0	0
Fe <sup>3+</sup> ...	.009	.02	.04	Fe <sup>3+</sup> ...	TA or P	.05	.06
Ga <sup>3+</sup> ...	.5	.05	.05	Ga <sup>3+</sup> ...	.3	0	.002
Hg <sup>2+</sup> ...	1	P	.2	Hg <sup>2+</sup> ...	TA	P	1
K <sup>+</sup> .....	.1	.04	.03	K <sup>+</sup> .....	.03	.001	.001
Li <sup>+</sup> .....	.02	.01	.01	Li <sup>+</sup> .....	TA	0	0.007
Mg <sup>2+</sup> ...	.03	0	0	Mn <sup>2+</sup> ...	.03	0	.002
Mn <sup>2+</sup> ...	.06	.001	.001	Na <sup>+</sup> ....	0.5	0	.003
Na <sup>+</sup> ....	.02	0	.002	NH <sub>4</sub> <sup>+</sup> ...	.03	ND	.003
NH <sub>4</sub> <sup>+</sup> ...	.05	0	.01	Ni <sup>2+</sup> ...	.03	0	.003
Ni <sup>2+</sup> ...	.04	0	0	Pb <sup>2+</sup> ...	5	P	P
Pb <sup>2+</sup> ...	2	P	P	Tl <sup>+</sup> .....	.7	P	.7
Tl <sup>+</sup> .....	.2	P	.06	Zn <sup>2+</sup> ...	TA or P	0	.004
VO <sup>2+</sup> ...	.5	.05	.05				
Zn <sup>2+</sup> ...	.1	.01	.01				

ND Not determined.

P Precipitated.

TA Total adsorption.

<sup>1</sup>Cation-exchange crystals, 20-50 mesh; Bio-Rad, control No. 10481.

TABLE A-1. - Distribution coefficients ( $K_d$ ) multiplied by  $10^{-3}$ ---Continued

Ion	H <sub>2</sub> O	0.1N HCl	0.1N H <sub>2</sub> SO <sub>4</sub>	Ion	H <sub>2</sub> O	0.1N HCl	0.1N H <sub>2</sub> SO <sub>4</sub>
CERIUM PHOSPHATE				ZIRCONIUM ARSENATE			
Ag <sup>+</sup> ....	0.4	P	P	Ag <sup>+</sup> ....	.05	P	P
AsO <sub>4</sub> <sup>3-</sup> ..	.005	0.01	0.009	Al <sup>3+</sup> ....	.1	0	0
Ca <sup>2+</sup> ....	.02	0	0	Cd <sup>2+</sup> ....	.02	0	0
Cd <sup>2+</sup> ....	.01	0	0	Co <sup>2+</sup> ....	.01	0	0
Hg <sup>2+</sup> ....	.1	P	.03	Cr <sup>3+</sup> ....	.3	.007	.02
K <sup>+</sup> ....	.2	.04	.01	Cu <sup>2+</sup> ....	.03	.004	.003
Mn <sup>2+</sup> ....	.01	.001	.008	Fe <sup>3+</sup> ....	TA or P	.2	.4
Na <sup>+</sup> ....	.03	.005	.004	Ga <sup>3+</sup> ....	2	.01	.03
NH <sub>4</sub> <sup>+</sup> ....	.06	.002	.03	Hg <sup>2+</sup> ....	5	P	.5
Pb <sup>2+</sup> ....	.03	P	P	K <sup>+</sup> ....	0.02	.009	.01
Tl <sup>+</sup> ....	.6	P	.1	NH <sub>4</sub> <sup>+</sup> ....	.02	.002	.02
				Pb <sup>2+</sup> ....	.4	P	P
				PO <sub>4</sub> <sup>3-</sup> ..	TA	TA	TA
				Tl <sup>+</sup> ....	.1	P	.05
				VO <sup>2+</sup> ....	.1	.009	.009
				Zn <sup>2+</sup> ....	.01	.001	.001
COMMERCIAL CERIC TITANATE <sup>1</sup>				THORIUM ARSENATE, Th(HAsO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O			
Ga <sup>3+</sup> ....	0.02	0	0	Ca <sup>2+</sup> ....	3	TA	2
Hg <sup>2+</sup> ....	.03	P	.007	Hg <sup>2+</sup> ....	.001	0.01	.004
Pb <sup>2+</sup> ....	.04	P	P	VO <sup>2+</sup> ....	TA	TA	TA
COMMERCIAL AMMONIUM MOLYBDOPHOSPHATE <sup>2</sup>				TITANIUM TUNGSTATE			
Ag <sup>+</sup> ....	0.04	P	P	Ag <sup>+</sup> ....	.08	P	P
Al <sup>3+</sup> ....	.01	0.04	0.03	AsO <sub>4</sub> <sup>3-</sup> ..	.002	0.01	0.008
Ca <sup>2+</sup> ....	.03	.02	.02	Cu <sup>2+</sup> ....	.01	.004	.003
Cd <sup>2+</sup> ....	.03	.02	.01	Hg <sup>2+</sup> ....	.09	P	.02
Co <sup>2+</sup> ....	.04	.02	.02	K <sup>+</sup> ....	.03	.01	.01
Cr <sup>3+</sup> ....	.09	.05	.04	Li <sup>+</sup> ....	0.01	.005	.005
Cu <sup>2+</sup> ....	.04	.02	.01	NH <sub>4</sub> <sup>+</sup> ....	.03	.01	.02
Fe <sup>3+</sup> ....	P	.04	.03	Pb <sup>2+</sup> ....	.07	P	0
Ga <sup>3+</sup> ....	.1	.05	.04	PO <sub>4</sub> <sup>3-</sup> ..	0	.01	.005
Hg <sup>2+</sup> ....	.4	P	.4	Tl <sup>+</sup> ....	.4	P	.1
K <sup>+</sup> ....	.02	.02	.02				
Mg <sup>2+</sup> ....	.03	.02	.02				
Mn <sup>2+</sup> ....	.03	.02	.02				
Ni <sup>2+</sup> ....	.04	.02	.02				
Pb <sup>2+</sup> ....	TA or P	P	P				
Tl <sup>+</sup> ....	TA	P	TA				
VO <sup>2+</sup> ....	.2	.02	.02				
Zn <sup>2+</sup> ....	.04	.03	.02				
ZIRCONIUM TUNGSTATE				CERIUM TUNGSTATE			
Ag <sup>+</sup> ....	0.02	P	P	Ag <sup>+</sup> ....	0.03	P	P
Ca <sup>2+</sup> ....	.01	0.01	P	AsO <sub>4</sub> <sup>3-</sup> ..	.1	0.4	0.1
Cu <sup>2+</sup> ....	.01	0	0	Cr <sup>3+</sup> ....	.04	0	0
Hg <sup>2+</sup> ....	.02	P	.01	Fe <sup>3+</sup> ....	.4	.01	.03
Li <sup>+</sup> ....	.02	.02	.01	Ga <sup>3+</sup> ....	.05	0	.002
Pb <sup>2+</sup> ....	.04	P	P	Hg <sup>2+</sup> ....	1	P	.02
PO <sub>4</sub> <sup>3-</sup> ..	.006	.01	.006	K <sup>+</sup> ....	.03	.005	.009
Tl <sup>+</sup> ....	.05	P	.03	Pb <sup>2+</sup> ....	.2	P	P
				PO <sub>4</sub> <sup>3-</sup> ..	TA	1	.05
				Tl <sup>+</sup> ....	.06	P	.05
				VO <sup>2+</sup> ....	.1	.04	.03

ND Not determined. P Precipitated. TA Total adsorption.

<sup>1</sup>Powder; Alfa Products, stock No. CE-104.<sup>2</sup>Bio-Rad, control No. 13827.

TABLE A-1. - Distributed coefficients ( $K_d$ ) multiplied by  $10^{-3}$ --Continued

## Copper Ferrocyanide

Ion	H <sub>2</sub> O	0.1N HCl	0.1N H <sub>2</sub> SO <sub>4</sub>
Ag <sup>+</sup> ....	9	P	P
AsO <sub>4</sub> <sup>3-</sup> ..	.03	0.008	0.006
Ca <sup>2+</sup> ...	.01	.002	.002
Cd <sup>2+</sup> ...	.02	.004	.004
Co <sup>2+</sup> ...	.02	.001	.002
Cr <sup>3+</sup> ...	3	0	0
Ga <sup>3+</sup> ...	3	.02	.01
Mn <sup>2+</sup> ...	.01	0	.001
Ni <sup>2+</sup> ...	.02	.003	.003
Pb <sup>2+</sup> ...	.02	P	P
PO <sub>4</sub> <sup>3-</sup> ..	.03	.005	0
Tl <sup>+</sup> ....	TA	P	.05
VO <sup>2+</sup> ...	.03	.01	.01
Zn <sup>2+</sup> ...	.02	.004	.004

P Precipitated.

TA Total adsorption.

Aluminum Hydroxy Sulfate, Al(SO<sub>4</sub>)OH

Ion	H <sub>2</sub> O	0.1N H <sub>2</sub> SO <sub>4</sub>	0.1N NaOH
Ag <sup>+</sup> ....	0.02	0	P
AsO <sub>4</sub> <sup>3-</sup> ..	.04	0	0.2
CN <sup>-</sup> ....	.1	D	.05
Ga <sup>3+</sup> ...	.8	0	7
Hg <sup>2+</sup> ...	.3	0	P
Li <sup>+</sup> ....	0	0	.5
Na <sup>+</sup> ....	.02	0	SI
Pb <sup>2+</sup> ...	6	0	TA or P
PO <sub>4</sub> <sup>3-</sup> ..	.1	0	TA
VO <sup>2+</sup> ...	.009	0	1
Zn <sup>2+</sup> ...	0	.01	P

D Decomposed or dissolved.

P Precipitated.

SI Solvent interference.

TA Total adsorption.

## Hydrous Ferric Hydroxide

Ion	H <sub>2</sub> O	0.1N HNO <sub>3</sub>
AsO <sub>4</sub> <sup>3-</sup> ..	0.2	0.2
Cd <sup>2+</sup> ...	.06	.07
Co <sup>2+</sup> ...	.07	.05
Hg <sup>2+</sup> ...	.4	.4
Li <sup>+</sup> ....	.01	.006
Pb <sup>2+</sup> ...	.5	.3
PO <sub>4</sub> <sup>3-</sup> ..	.8	.9